

PATENT ABSTRACTS OF JAPAN

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(54) SURFACE TREATMENT METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To impart antifouling, dustproof, waterproof and moistureproof properties, rust preventiveness, etc., to the surface of a substrate and to maintain these characteristics even in a severe service environment by treating the surface of the substrate with a compd. contg. Si, Al or Ti.

SOLUTION: The compd. used for surface treatment is represented by the formula $R_nX(OR')^{m-n}$, wherein R is alkyl, alkenyl or phenyl, R' is alkyl, X is Si, Al or Ti, $0 \leq n \leq 3$, $m=3$ in the case of Al and $m=4$ in the case of Si or Ti. An organoalkoxysilane or organosilanol obtd. by hydrolyzing it, e.g. monomethyltrimethoxysilane is suitable for use as the silicon compd. A trialkoxy-aluminum compd. or its hydrolyzate is suitable for use as the aluminum compd. An organoalkoxy-titanium or organotitanol obtd. by hydrolyzing it is suitable for use as the titanium compd.

[Claim(s)]

[Claim 1] general formula $R_nX(OR')_{m-n}$ (however, the inside R of a formula -- an alkyl group.)

An alkenyl group or a phenyl group, and R' express an alkyl group, and X expresses silicon, aluminum, or titanium, A surface treatment method with which $n=0-3$ and aluminum are characterized by a thing for which $m=3$, silicon, or titanium was chosen from compounds shown by $m=4$, or these hydrolysis products, and which process a kind to a base material surface at least.

[Claim 2] A surface treatment method characterized by X being silicon in a general formula of claim 1.

[Claim 3] A surface treatment method characterized by X being aluminum in a general formula of claim 1.

[Claim 4] A surface treatment method characterized by X being titanium in a general formula of claim 1.

[Claim 5] A surface treatment method carrying out ground treatment of the base material surface by one to claims 1-4 of methods, and performing finishing processing on it.

[Claim 6] A surface treatment method using a silicone compound or its derivative as finishing processing of claim 5.

[Claim 7] A surface treatment method using a fluorine compound or its derivative as finishing processing of claim 5.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]In this invention, the base material surface of metal, glass, pottery, paper, resin, etc. is processed.

Therefore, a surface treatment method which gave surface characteristics, such as antifouling property, protection-against-dust nature, waterproofness, dampproofing, rust prevention, lubricity, a mold-release characteristic, contamination detachability, and water and oil repellency, to the base material surface, and was excellent in the endurance of these characteristics.

[0002]

[Description of the Prior Art]Conventionally, metal finishing is mainly the purpose of rust prevention and corrosion prevention, and chemical conversion has been performed. For example, alumite film processing etc. are performed to phosphoric acid coating treatment and an aluminum board in the steel plate or the zinc side. Various pretreatments are tried for coating etc. Such coating treatment is rust prevention of a steel plate and an aluminum board and processing of the purposes with a main surface protection. It is known that various kinds of coupling agents and metallic oxides generally have an effect in the adhesive improvement in the surfaces, such as metal. It is publicly known to give non cohesiveness by heat-treatment of a fluoro-resin etc. However, for example about the superiors for the antifouling property of the surfaces, such as stainless steel and glass, an adhesive property, or paintwork, simple surface treatment art is not established enough. Not only metal but the surface characteristic which was generally excellent in endurance to the scarce substrate of adhesion is given, and the disposal method which can be hardened also by ordinary temperature with the thin tunic which was moreover excellent in compactness is not known.

[0003]

[Problem(s) to be Solved by the Invention] Like the above, conventionally, the thin tunic which has endurance in the adhesive usually scarce base material surface of metal, such as stainless steel and aluminum, glass, pottery, paper, resin, etc. was not able to be made, and, moreover, the tunic was not able to be processed by room temperature setting. This invention was solved about this point by processing based on the reaction which improves an adhesive property by processing with the skillful combination of this ground treatment and a finishing agent again. And surface-characteristic grant of antifouling property, protection-against-dust nature, waterproofness, dampproofing, rust prevention, lubricity, a mold-release characteristic, contamination detachability, water and oil repellency, etc. was enabled in the base material surface, and the surface treatment method which was excellent in the endurance of these surface characteristics under the cruel operating environment was found out. And it is the tunic excellent in very thin transparent compactness, and has the feature made good [room temperature setting].

[0004]

[Means for Solving the Problem] Said technical problem of this invention is attained in a compound containing silicon, aluminum, or titanium independent or by processing a base material surface using two or more mixtures. They have a good compound which an alkoxy group or an OH radical mainly coupled directly with silicon, aluminum, or a titanium atom. A hydrogen bond is carried out to a base material surface by these, and a tunic is formed by a condensation reaction. Furthermore, the effect is more notably attained by making this into a ground by performing finishing processing with a silicone compound or fluorine compounds, and these derivatives on it.

[0005] Organosilanol produced by generally hydrolyzing organoalkoxysilane or this as a silicon compound is suitable. A reaction is accelerable according to heating or a catalyst. Acid, alkali, or organic amine can be used as a catalyst. as an organic amine catalyst -- a tertiary amine -- electric dissociation exponent -- eight or more -- especially -- nine or more -- **** -- better -- **. The organosilanol can use what is obtained by other natural processes. For example, when water is contacted in an ORUGANO halo silane, it is the method of causing a hydrolysis reaction and generating a silanol compound. As organoalkoxysilane, for example Monomethyl trimethoxysilane, Dimethyldimethoxysilane, trimethylmethoxysilane, a tetramethoxy silane, It is monoethyl triethoxysilane, diethyldiethoxysilane, a tetraethoxysilane, methylethyl dimethoxysilane, monophenyl trimethoxysilane, etc., in addition a silane coupling agent can also be mentioned. These serve as organosilanol by hydrolysis. As organosilanol, generally it is expressed with $R_n Si(OH)_{4-n}$, R is an alkyl group, an alkenyl group, or a phenyl group here, and n is 0-3. For example, a monomethyl silanol, dimethyl silanol, a trimethyl silanol, A silanol (tetra hydroxy silane), a monoethyl silanol, A diethylsilanol, triethyl silanol, a monopropyl

silanol, a dipropylsilanol, a TORIPURO pill silanol, a triisopropyl silanol, diphenylsilanediol, etc. can be mentioned. By heating or *****, the hydrogen bond of the organosilanol is carried out easily in a base material surface, and a firm tunic is further formed of a condensation reaction. A reaction advances also at ordinary temperature.

[0006]In an aluminium compound, a tunic is formed in a base material surface like a case of a silicon compound with for example, Tori trialkoxy aluminum compounds and these hydrolysis products (TORIHAIDOROKISHI aluminum), for example, aluminium hydroxide etc. in addition - as the Tori trialkoxy aluminum compound -- triisopropoxy aluminum, mono- sec-butoxydiisopropylaluminum, and TORIE -- an ibis -- sial minium etc. are mentioned. An aluminate coupling agent can also be used.

[0007]Like a silicon compound, as a titanium compound, are ORGANO alkoxy titanium and this ORGANO Chita Knoll produced by hydrolyzing, and as ORGANO alkoxy titanium, For example, monomethyl trimethoxytitanium, dimethyldimethoxytitanium, It is trimethyl monomethoxy titanium, tetramethoxy titanium, tetraisopropoxy titanium, tetra propoxytitanium, tetra-n-butoxytitanium, tetraethoxytitanium, diphenyldimethoxytitanium, etc., in addition a titanium coupling agent can also be mentioned. As ORGANO Chita Knoll, it is expressed with a general formula of $R_n Ti(OH)_{4-n}$, R is an alkyl group, an alkenyl group, or a phenyl group here, and n is

0-3. For example, mono- MECHIRUTORI hydroxy titanium, dimethyl dihydro KISHICHITAN, trimethyl hydroxy titanium, tetra hydroxy titanium, mono- ECHIRUTORI hydroxy titanium, mono- PUROIPIRUTORI hydroxy titanium, diphenyltitaniumdiol, etc. can be mentioned.

[0008]Formation of a tunic has a firmer direction with many OH radicals which the OH radical of these compounds can consider film formation by a hydrogen bond between OH radicals of a base material surface, and are generated by hydrolysis. Namely, $RSi(OH)_3$, $Si(OH)_4$, $aluminum(OH)_3$. By carrying out a hydrogen bond in a base material surface, and carrying out still more prompt condensation reaction or crosslinking reaction, a firmer tunic is formed and $RTi(OH)_3$ or $Ti(OH)_4$ shows a finishing agent and firm unity.

[0009]As for concentration of these compounds, 0.1 to 20 % of the weight is preferred, and as the solvent Alcohols, For example, methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, etc. can use a common organic solvent of paraffin hydrocarbon or aromatic hydrocarbon, for example, n-hexane, toluene, chlorobenzene, etc., and these mixtures may be sufficient as them. When using these compounds as two or more sorts of mixtures furthermore, the mixing ratio can choose arbitrary ratios. The tunic can obtain with a brush etc. liquid adjusted to predetermined concentration by spreading, spraying or immersion, etc., and a tunic is formed by air-drying or heat-treating this. Thus, although it is one special feature that it can harden also at ordinary temperature, heat-treatment has an effect which forms a tunic more nearly promptly.

[0010]By adding an organic amine system catalyst etc., a reaction is accelerated and film formation can be done easily. An organic amine system catalyst is a tertiary amine, and eight or more things have effective dissociation-constant-of-acid electric dissociation exponent, and it is still more preferred. [of nine or more things]

[0011]Coating treatment of the object substrate can be carried out to resin, such as metal, such as stainless steel, an aluminum board, and a griddle, PET, polypropylene, polyethylene, polystyrene, vinyl chloride, BOBARU, nylon, and ABS, a film, textiles (nature, composition), paper, glass, pottery, etc. By performing finishing processing of a silicone compound, fluorine compounds, or these derivatives on it by making the above-mentioned processing into ground treatment again, this invention can improve said characteristic of ground treatment more, can employ it efficiently, and can also give a various function of these finishing processing [itself] further. Of course, the adhesion of this ground treatment layer and a finishing treating layer is also excellent, and there is no problem also in endurance on a severe service condition. When performing finishing processing of a silicone compound, it can also be made a bilayer or multilayer coating beyond it using a silane compound of a silane coupling agent or others, polyorganosiloxane, reactive silicone, etc. As a silane coupling agent, for example 3-glycidoxypyltrimethoxysilane, 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, 3-aminopropyl triethoxysilane, N-phenyl-3-aminopropyl trimethoxysilane, etc. can be mentioned.

[0012]By the method as a silicone compound that a fluorine compound is also the same, finishing processing of a fluorine compound can be performed on the above-mentioned ground treatment. As a fluorine compound or its derivative, omega hydro-perfluoro alcohol of general formula $H(CF_2CF_2)_nCH_2OH$ (however, inside $n=1-6$ of a formula), etc. Perfluoro alcohol, perfluoro (meta) acrylate and those oligomer, other perfluoro acid ester, perfluoroalkyl silanes, etc. can be mentioned. By adding a silicon compound to a fluorine compound or its derivative, the effect can be further heightened as a hybrid. A result good [as a silicone compound] with a hardened type or denaturation type silicone in addition to the usual silicone types, such as oil and a varnish, is obtained. For example, denaturation type silicone with an end or side chains, such as an amino type, aminopolyether, epoxy, epoxy polyether, carboxyl, and carbinol, can be used.

[0013]As a practical example of a surface treatment in connection with these this inventions, processing of antifouling, such as a gas range made from stainless steel, a gas range pan, an iron pot, and wallpaper of vinyl chloride, antifouling of a stainless steel plate or an aluminum sash, etc. can be mentioned. For example, if this thing is applied to that cutting plane when carrying out cut processing of the aluminum board by which alumite processing was carried out, it is effective for corrosion prevention etc. In addition, this thing can be applied to tile joints of a bath, or a coil of a waterworks, and water proof, rust prevention, and an antifouling effect can be heightened. A water resisting property can be given to a poval film of hydrophilic

nature.

[0014]Next, an example explains still in detail.

[0015][Example 1] 3 g of ethyl orthosilicate (tetraethoxysilane) is taken to a 100-cc beaker, the chloride 4.1 g is further added for this gradually 2% with the ethyl alcohol 3g, and ethyl orthosilicate is hydrolyzed. Under the present circumstances, in order to make a reaction advance promptly, it adds, agitating 1 g of organic amino ***** 10%. As this hydrolysis product, a tetra hydroxy silane or its derivative is obtained, and let what diluted this with ethyl alcohol to 3% of predetermined concentration be A-ground treatment agent 1 liquid. Four unsettled stainless steel plates (0.5 mm in thickness) into which a base material surface is not processed were cut in size of 50x100 mm using this A-1 liquid, and it applied to homogeneity with a brush on that surface, respectively. Two of four applied sheets were dried at a room temperature for about 1 hour, remaining two sheets were dried at 160 ** with a homiothermal electric furnace for 30 minutes, and a coat was hardened, respectively. On the other hand, a perfluoro alkoxy silane compound made from Sannan Composition is hydrolyzed into 10g picking and this by adding an organic amine system catalyst like the above with chloride of theoretical reacting weight as a finishing agent, and let the resultant be B-finishing agent 1 liquid. This B-1 liquid is diluted with an alcoholic mixture which makes an ethanol solution a subject to 10% of predetermined concentration. In order to improve familiarity by ground treatment furthermore, 2.5 g was added for room-temperature-setting type reactive silicone by Shin-Etsu Chemical Co., Ltd. Subsequently, after the above-mentioned A-1 liquid spreading, stoving was carried out at room temperature desiccation and 160 ** for 30 minutes, respectively, it applied B-1 liquid each to one thing which the first pass hardened as a secondary layer, a homiothermal electric furnace performed processing at 160 ** for 30 minutes, and it was considered as a test sample, respectively. About 2 g of pulp of a banana was rubbed against a test sample plate of four sheets, respectively, and it carbonized at 160 ** for 30 minutes. After carbonization, when it cooled to a room temperature, pulp of an adhering portion, i.e., a carbonized banana, was lightly extruded at the point of a spatula, and the detachability was compared. Each always graded simultaneously by 4-5 persons, and evaluation took average value except for the greatest and minimum result. The result is shown in the 1st table.

[0016][Comparative example] An unsettled stainless steel plate (0.5 mm in thickness) was cut in size of 50x100 mm, and the surface was not processed at all, and like Example 1, about 2 g of pulp of a banana was rubbed, and it heated for 30 minutes at 160 ** with a homiothermal electric furnace. After calcination, when it cooled to a room temperature, it carbonized, pulp of an adhering banana was lightly extruded at the point of a spatula, and the detachability was investigated. Each always graded simultaneously by 4-5 persons, and evaluation took average value except for the greatest and minimum result. The result is shown in the 1st table.

[0017][Example 2] As a ground treatment agent in Example 1, in addition to a tetra hydroxy silane, tetra hydroxy titanium and a mixture with the former were used, and a detachability test in pulp carbide of a banana was done like Example 1. Used tetra hydroxy titanium is the organic titanate TBT (tetra-n-butoxytitanium) and TPT (tetraisopropoxy titanium) by Nippon Soda Co., Ltd., and used isopropyl alcohol for a solvent. It compared that it was unsettled and the result was shown in the 2nd table.

[0018][Example 3] In order to evaluate the endurance of detachability, after detachability test ending with a stainless steel plate in Examples 1 and 2, carbide which immersed a test piece in about 40 °C warm water tub, and adhered was ground lightly, and was removed, and Ox estimated sensuously the ease of removing of an affix in that case. Subsequently, about 2 g of pulp of a banana was again rubbed for these like the above after washing desiccation, and 160 °C estimated the detachability of an affix after 30-minute heat-treatment. This was repeated 10 times and the same evaluation was shown in the 3rd table each time.

[0019]Subsequently, by hydrolysis of ORGANO alkoxy titanium, film formation was carried out to a base material surface, a paint was applied to the surface, a comparative examination was tried and the ease of the ability to take was shown in Example 4.

[0020][Example 4] The organic titanate TBT (tetra-n-butoxytitanium) by Nippon Soda Co., Ltd., since it dilutes with isopropyl alcohol to 3% -- this -- each of a stainless steel plate unsettled 0.3 mm in thickness of 40 mm squares with a brush, the 0.5-mm aluminum board in thickness, and a 1.3-mm glass plate -- heated on the surface for 30 minutes at 160 °C, it was made to harden a coat after spreading uniformly, and ground treatment was carried out. Subsequently, a spray for marking by Nippon Paint Co., Ltd. "NIPPE home paint" (alkyd resin) was applied to each specimen which performed the above-mentioned ground treatment, and it was air-dry. Length, width, and 11 each were minced for a slot of parallel lines which reach a base to a grid at intervals of 1 mm using a knife sharp to this coat, and 100 grids (10x10) were made. Moreover a Scotch tape by Nichiban Co., Ltd. (18-mm width) was made to stick by pressure, this was torn off promptly, and adhesion was evaluated among grids of 100 pieces with exfoliation or the number which there is no deficit in part and remained thoroughly (grid examination). Simultaneously, for comparison, a paint was applied to a thing without ground treatment of the organic titanate TBT like the above, and a grid examination was done on it. Those results were shown in the 4th table.

[0021]

第1表

比較 例	実験 NO.	第一層		第二層		剥離性 評価
		下地処理剤	硬化条件	上塗り剤	硬化条件	
1		未処理 (生地のまま)	—————	な し	—————	×
実 施 例	2	A-1液 3%	室温風乾	な し	—————	○
	3	A-1液 3%	160℃×30分	な し	—————	○
	4	A-1液 3%	室温風乾	B-1液 10%	160℃×30分	◎
	5	A-1液 3%	160℃×30分	B-1液 10%	160℃×30分	◎

基材：ステンレス鋼板

A-1液

： テトラヒドロキシシランアルコール溶液

B-1液 ： パーフルオロアルコキシシラン加水分解生成物
アルコール溶液

剥離性評価

◎ 全体的に容易に剥がれる

○ やや剥がれにくい

× ほとんど剥がれない

第2表

比較例	実験 N O.	第一層		第二層		剥離性 評価
		下地処理剤	硬化条件	上塗り剤	硬化条件	
1		未処理 (生地のまま)	—	なし	—	×
実施例 2	6	A-2液 3%	室温風乾	なし	—	○
	7	A-2液 3%	160℃×30分	なし	—	○
	8	A-2液 3%	室温風乾	B-1液 10%	160℃×30分	○
	9	A-2液 3%	160℃×30分	B-1液 10%	160℃×30分	◎
	10	A-3液 3%	160℃×30分	B-1液 10%	160℃×30分	○
	11	A-1液/A-2液 3% 3%	160℃×30分	B-1液 10%	160℃×30分	◎

基材：ステンレス鋼板

※

A-2液：テトラヒドロキシチタン（TBT）アルコール溶液

A-3液：テトラヒドロキシチタン（TPP）アルコール溶液

B-1液：実施例1と同じ

※※

剥離性評価：実施例1と同じ

第3表

実験 N O.	第一層		第二層		剥離性の繰り返しテスト結果										総合評価
	下地処理	硬化条件	上塗り層	硬化条件	1	2	3	4	5	6	7	8	9	10	
1'	未処理	—	なし	—	△	△	×	×	×	×	×	×	×	×	×
5'	通 A-1液 3% ×30分	160℃ ×30分	通 B-1液 10% ×30分	160℃ ×30分	○	○	○	○	△	△	△	△	×	×	△
9'	通 A-2液 3% ×30分	160℃ ×30分	通 B-1液 10% ×30分	160℃ ×30分	○	○	○	○	○	○	○	△	△	△	○

基材 : ステンレス鋼板

実験N O. 1'、5'、9'は実施例1の実験N O. 1、5、9と同一処理条件

※

※※

A-1液 : 実施例1と同じ

剥離性の繰り返しテスト評価

A-2液 : 実施例2と同じ

○ 容易に剥離

B-1液 : 実施例1と同じ

△ やや剥がれにくい

× 剥がれにくい

() 内は温水槽浸漬後の炭化物の取れ易さ : ○ 取れ易い

× 取れにくい

※※※

総合評価

○ 繰り返し性優

△ 繰り返し性良

× 繰り返し性可

第 4 表

実験 NO.	基 材 種 類	第一層		第二層		剝離テスト (剥離目テスト)
		下地処理剤	硬化条件	上塗り剤	硬化条件	
実 施 例 4	ステンレス板	未処理	—	なし	—	0/100
	目上	※ A-2 液 3 %	160℃×30分	なし	—	100/100
	目上	※ A-3 液 3 %	160℃×30分	なし	—	100/100
	アルミ板	未処理	—	なし	—	25/100
	目上	※ A-3 液 3 %	160℃×30分	なし	—	100/100
	ガラス板	未処理	—	なし	—	20/100
	目上	※ A-3 液 3 %	160℃×30分	なし	—	90/100

A-2 液 : 実施例 2 と同様

A-3 液 : 同上

剥離

剥離テスト評価基準 : 剥離テストで完全に残った数/全体の数 (100ヶ)

[Translation done.]